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CHARACTERIZATION OF CHROMIC-ACID ANODIZED
2024-T3 ALUMINUM ADHERENDS

WILLIAM J. RUSSELL
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SEPTEMBER 1977



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CHARACTERIZATION OF CHROMIC-ACID
ANODIZED 2024-T3 ALUMINUM ADHERENDS

by

William Russell
Carolyn A. L. Westerdahl

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>The topography of 2024-T3 aluminum-alloy surfaces has been characterized by using high-magnification transmission electron microscopy (TEM) at various stages during the chromic-acid anodizing procedure used to prepare aluminum surfaces for adhesive bonding. The surface structure characteristic of the unsealed chromic-acid anodized alloy was found to form during the first 6 minutes of the 37½-minute anodizing cycle; the surface structure characteristic of the sealed anodized alloy was found to form during the last half of the 8-minute sealing cycle. The surface</p>														

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structure of FPL deoxidized and of unsealed anodized surfaces consists of a repeating pattern of close-packed depressions 200 to 800 angstrom units in diameter. The structure of the sealed surface consists of crevices 500 to 2,000 angstrom units wide between mounds of material formed during sealing.

The chemical composition of the surfaces was determined after anodizing and also after sealing the surface, using electron spectroscopy for chemical analysis and auger electron spectroscopy. These surfaces were found to consist of aluminum, oxygen, carbon, and nitrogen with traces of silicon and manganese. Copper and magnesium, two of the major alloying elements in the alloy used, were not detected.

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INTRODUCTION

The object of this investigation was to characterize a chromic-acid anodized aluminum surface prepared for adhesive bonding. This characterization was limited to the topmost layer of the surface which was the only part of the substrate in actual contact with the adhesive after bonding.

Aluminum, as received from the supplier or after fabrication, does not form strong durable joints when adhesively bonded. Durable joints can be obtained only after the surface of the metal has been properly cleaned and prepared for adhesive bonding. The optimum procedures used to clean and prepare these surfaces for adhesive bonding have been empirically determined. This was accomplished by preparing specimens in different ways, then adhesive bonding, and testing the joints to determine which processing conditions produce the strongest and most durable adhesive joints. The work here is a study of the surfaces produced by an empirically developed process in order to determine its characteristics.

Chromic-acid anodizing of aluminum is one process used for preparing a strong durable adhesive joint. Work done at this laboratory indicates that adhesive bonds made with chromic-acid anodized aluminum surfaces (2024-T3) are slightly more durable than those prepared using the FPL etch procedure (Method A of ASTM Standard D 2651-67) (Ref 1). Other authorities have reported similar results. Schliekelmann reports that the chromic-acid anodizing process as described under British Specification DTD 910C will yield satisfactory results in conjunction with adhesive bonding (Ref 2). Hockney compares the strength and durability of chromic-acid anodized aluminum adhesive joints protected by using a polysulfide sealant with sulfochromate-acid etched aluminum adhesive joints without a sealant. His results show the protected chromic-acid anodized joints to be superior (Ref 3). The data given by Cagle indicate that the chromic-acid anodized aluminum surfaces produce adhesive bonds with strength and durability equivalent to those produced with sulfochromate-acid etched surfaces. Cagle does not recommend the process because he does not consider the process as "a method of producing bonds of maximum expectation" (Ref 4 and 5). The varying reports in the literature suggest the possible existence of undefined variables in the anodizing process.

DISCUSSION

Study of Surface Topography

The chromic anodized surfaces studied in this work were made using the Bell Helicopter Company Process Specification BPS FW 4352 Rev E (Ref 6). The topography of the surface was examined with the transmission electron microscope after each step in the process. In this way the effect of each procedure upon the surface was noted. The chemical composition of the surface after the anodizing and sealing operations were completed was studied using auger and electron spectroscopy for chemical analysis. These techniques determined the chemical makeup of the surface material directly in contact with the adhesive.

The most direct way to study a surface is to look at it under sufficient magnification to bring out the structures of interest. It was found that magnification of approximately one hundred thousand diameters was required to see what was happening as the surfaces went through the various stages of processing. The required magnification was obtained using a transmission electron microscope. This instrument is unsuitable for study of the surface directly, since the specimens are opaque to the electron beam. Thus it was necessary to make very thin transparent copies of the surface (replicas). These were made by vacuum evaporating platinum or another heavy metal onto the surface at a low angle to bring out fine details of the surface structure and increase the contrast. The surface was then coated with a uniform film of vacuum-evaporated carbon. The films of material were freed from the surface by etching the metal out from underneath, after which they floated free. They were then rinsed and air dried. Replicas made in this manner are called single-stage replicas and are ready for study with the transmission electron microscope.

Degreasing

The metal when received from the supplier is contaminated with oil, dirt, and marking ink. It is also covered with a continuous film of aluminum oxide approximately 165 angstrom units thick (Ref 7). The oxide film is formed during rolling and heat treating operations when sheets of the required thickness and strength are fabricated. The first step in the chromic-acid anodizing process is to vapor degrease the surface by flushing the oil and dirt from the specimen with solvent, the vapors of which condense to a liquid on the cool metal. Figures 1 and 2 are TEM micrographs of an acetone-degreased surface. Figure 1 is at relatively low magnification and shows the structure of the oxide surface.

Alkaline Cleaning

After degreasing to remove all solvent soluble contaminants, the metal is immersed in alkaline cleaner to remove all water soluble and saponifiable soils. This cleaner can be either inhibited or noninhibited. The noninhibited cleaner etches the surface of the metal removing the oxide layer as well as the water soluble surface contaminants. The inhibited cleaner contains silicates or other additives that either prevent or minimize the etching of the surface by the cleaner. The noninhibited cleaner was used for this work.

When some aluminum alloys are alkaline etched, a film of black powdery material or smut is formed on the surface of the metal. The smut does not rinse off and has to be removed before a true replica of the underlying surface can be made. This was done by making a series of casts of the dried surface using solvent-softened plastic replicating tape. After the solvent had evaporated and the casts or plastic replicas had hardened, they were stripped off the surface. This technique removed the dried powdery material without damaging or changing the surface of the metal. The procedure was repeated until all the foreign material was removed and the surface was clean. A final careful plastic cast of the cleaned surface was then made. This was used to make a two-stage replica of the surface.

When the replicas were studied, the alkaline-cleaned surface was found to be reasonably smooth. All traces of the roll marks on the degreased surface had been removed by the cleaner. Crevices noted in the surface were probably sites where ridges of oxide had become entrapped or embossed into the surface of the metal during fabrication. When the oxide was dissolved out during alkaline cleaning, a void was left. Figure 3 is a low-magnification micrograph showing the voids. When studied at a higher magnification, the surface appears to have a wave-like pattern with random shallow pits approximately 200 angstrom units in diameter (Fig 4).

Deoxidizing

After the metal was alkaline cleaned, it was immersed in a deoxidizing bath consisting of a hot solution of sulfuric acid and sodium dichromate in water. When the specimens covered with the black smut were placed in the deoxidizing bath, the smut dissolved and normal etching

proceeded. Figure 5 shows the surface pattern that developed after 9 minutes in the deoxidizer. The pattern consists of etched-out depressions (concave) about 2 to 3 microns in diameter. When the structure of the surface within these etched out depressions is examined at higher magnification (Fig 6), a dimpled concave sub-structure is seen. These irregular shaped dimples are 400 to 800 angstroms in diameter. The surface structures shown in Figures 5 and 6 are typical of 2024-T3 alloy surfaces etched in the sulfochromate deoxidizer whether the surface has been alkaline etched or only solvent degreased prior to processing (Ref 8). When specimens which have been degreased but not alkaline cleaned are immersed in the deoxidizer, the oxide layer dissolves away within the first 1/2 minute of processing. After this the metal is etched, developing a surface structure typical of the etchant-alloy combination (Ref 9). The typical surface structure is the same as that shown in Figures 5 and 6. Thus it appears that treatment prior to deoxidizing has no visible effect on the surface structure developed in the deoxidizing solution.

Anodizing

The anodizing cycle as described in the process specification is a complex procedure requiring specified increases in the anodizing voltage during a given time sequence. Specimens were removed at various times during the cycle to determine if changes in the voltage and time of anodizing had any effect on the surface structure.

Previous transmission electron microscopy (TEM) studies of anodized coatings used specimens of the coating obtained by dissolving the aluminum substrate underneath the coating, leaving the oxide layer intact (Ref 10). The oxide was sufficiently thin to be used as a specimen. This procedure had two disadvantages for our purposes. It revealed the internal structure of the coating, not the surface, and there was no assurance that the technique used to dissolve the metal did not alter the sample surface. Thus anodized surfaces were replicated using the single-stage process previously described. This procedure enabled detailed study of the surface at maximum resolution and also assured that minimal changes were occurring as a result of the replicating process.

Figure 7 is a high magnification TEM micrograph showing the structure of the surface after the first two minutes (at $7\frac{1}{2}$ volts) of anodizing. This figure shows a surface structure that is in transition between the structure developed in the deoxidizer (Fig 6) and the fully developed anodized

structure. The structure of the deoxidized surface shown in Figure 6 is becoming obscure or indistinct, and the structure shown in Figure 8 is beginning to emerge.

Figure 8 is a high magnification TEM micrograph of the structure of the surface after $2\frac{1}{2}$ minutes (at $7\frac{1}{2}$ volts) of anodizing. The structure in this figure has become almost typical of the unsealed chromic-acid anodized surface. Figure 9 shows the surface after $5\frac{1}{2}$ minutes of anodizing ($22\frac{1}{2}$ volts max). All traces of the surface structure typical of the deoxidized surface have disappeared. No Additional change appears to occur during the remainder of the anodizing cycle other than a possible deepening of the pores. Figure 10 shows the surface after anodizing has been completed (35 minutes at 40 volts). A careful comparison of Figure 8 ($2\frac{1}{2}$ minutes, Figure 9 ($5\frac{1}{2}$ minutes), and Figure 10 (35 minutes) shows that the surface structure during the latter part of the anodizing cycle is essentially the same even to the size of the pores. The pores appear as dimples or conical depressions in the surface. The only change that can be detected during the latter part of the anodizing cycle is a possible increase in the depth of the pores. This change is difficult to measure, since we are working at the limiting resolution of the microscope with carbon platinum replicas. Since it was impossible to determine the structure of the interior of the pores using the single-stage replicating process (Fig 10), a two-stage replica was made. A cast of the surface was taken using solvent-softened plastic replicating tape. This cast was the inverse of the surface. It was convex where the anodized surface was concave and concave where it was convex. Thus, the pores in the anodic coating were reproduced as spikes protruding from the surface of the plastic cast. When the cast was replicated and examined with the TEM, the pores were found to be truncated cone-like hollows in the anodic coating. These were narrow at the base, opening up as they approached the surface. Figure 11 is a micrograph showing the structure of the pores using a two-stage replica.

Sealing

After anodizing has been completed, the surface is frequently immersed in a hot dilute solution of chromic acid to seal the pores and improve the corrosion resistance of the coating. The mechanism of the sealing process is described by Barkman as a swelling of the aluminum oxide on the surface of the coating (Ref 10). This prevents corrosive attack upon the underlying metal. Figure 12 shows the surface of a sealed anodized specimen. This is a micrograph of a surface that has undergone the complete anodizing and sealing procedures defined by the Bell Process Specification (Ref 6). As can be seen, the surface is radically different from

an unsealed anodized surface. The pore structure shown in Figure 10 is completely covered by a material that appears to have been extruded from the pores, forming a pattern of hills and ridges. Thus the sealing operation not only seals and closes the pore structure, it actually develops a definite surface structure distinctly different from the unsealed anodized surface.

Figure 13 is a micrograph of the sealed surface prepared in a slightly different manner. The area was selected to show the structure of the extruded material. The sphere in the lower left corner is a 0.3-micrometer-diameter latex particle which was used to interpret surface structure and determine surface profile.

When specimens that had been anodized and sealed for one-half the normal 4-minute cycle were examined, the surface structure was found to be very similar to that of an unsealed specimen. When a two-stage replica was made and examined, the surface of the specimen sealed for one-half the normal cycle was again found to be similar to the unsealed specimen. The internal structure of the pore was apparently unaltered. Thus it appears that the material found on the surface of the sealed anodic coating forms during the last half of the sealing cycle. This indicates that strict control of the sealing solution, composition, temperature, and time of processing are critical. Slight changes may have a significant effect.

The differences that occur in the surface structure of the specimens as a result of the deoxidizing, anodizing, and sealing operations are evident at only very high magnifications. At lower magnification the structure of these surfaces is very similar to that shown in Figure 5.

Surface Profile

There is difficulty in interpreting the topography of a surface with TEM. Optical illusions are frequently encountered, and it is impossible at times to determine whether a structure is concave or convex. As an aid for this determination, the specimens under study were sprayed with a latex solution prior to replicating. This deposited spheres of latex onto the surface. Since the spheres of necessity had to be convex, it was possible to interpret the surface by using the spheres as a reference. With the spheres as a guide, profiles of five of the surfaces were roughly drawn to scale (Fig 14).

The profiles of the first two surfaces are notable in that they are not repetitive. The surface structures, although distinctive, are random. The surface of the degreased specimen is fairly smooth with gradual changes in slope over distances of a half micron or more. The surface of the alkaline etched specimen was also non-repetitive, although there was evidence of a wave-like pattern. The surface profile of the deoxidized specimen was drawn from Figure 6. This surface consists of a repetitive pattern of small cup-like depressions or dimples. The cups, although random in shape, are of a fairly consistent size (from 200 to 400 angstroms) in diameter and are closely packed. The profile of the unsealed anodic coating was drawn after a careful study of Figures 10 and 11. As can be seen from the profile, this surface also consists of a repetitive pattern of depressions. These are small pores in the coating whose diameter at the surface is about 200 to 300 angstroms with a secondary pattern of larger pores whose diameter at the surface is 400 to 800 angstroms.

The profile of the sealed anodic coating was sketched from Figure 13. The structures on this surface consist of a series of piles or lumps of material that appear to have come out of the pores. It is again noted that these structures have a diameter of 400 to 1000 angstroms. In this case however, the structures are convex.

The last three surfaces described are used as substrates for durable adhesive joints. They were found to consist of a repetitive pattern which at least in two cases is concave. In the case of the sealed coating which has convex lumps of material on the surface, the area between the lumps could be considered as concave depressions. The dimensions of these structures range from 200 to 1000 angstroms and all appear to have roughly the same depth. Thus it is entirely possible that a pattern of closely packed depressions 200 to 1000 angstroms wide and of about the same depth are characteristic of surfaces which are properly prepared for forming durable adhesive bonds.

Chemical Composition of the Surface

The chemical environment experienced by an adhesive on a surface is determined by the material which the adhesive actually contacts. The material immediately below the surface is not in contact with the adhesive and thus has little interaction with it. Therefore, an effort was made to determine the composition of the top-most layer. When the chemical composition of a surface is analyzed, the results obtained are frequently far different from the results expected. This is because small quantities of material

absorbed or reacted onto a surface can cover a large percentage of the total area and are effective to a degree far beyond that indicated by their mass.

ESCA Studies

Surfaces of sealed and unsealed chromic-acid anodized 2024-T4 aluminum specimens were studied using electron spectroscopy for chemical analysis (ESCA). This technique, which is also known as X-ray photo electron spectroscopy, yields information about the chemical composition of surfaces. X-rays incident to the surface being studied are used to knock out inner shell electrons from the surface atoms. Those electrons which are close enough to the surface to escape (0 to 50 angstroms) (Ref 11), are collected and their kinetic energy is analyzed. This energy is the difference between the energy imparted by the X-ray and the energy which bound the electron in the inner shell of the atom. The energy differences detected are unique for each element and thus provide a means of chemical identification. Since the kinetic energy of the electrons depends on the chemical bonding state of the element from which they come, this technique also yields some information on the type of chemical bonding to which the surface elements are subjected.

Table 1 is a tabulation of the results of studies showing the binding energy at which signal peaks were obtained, their relative intensities, and the elements from which they came. It will be noted that the results are reported as very very very strong to very very very weak. No numerical values are given. This is because the common methods of surface analysis (ESCA, Auger, SIMS, ISS) do not yield truly quantitative data (Ref 11). Table 2 is a listing of the bulk elemental composition of 2024 aluminum alloy, the material used in these experiments.

When the data in Tables 1 and 2 are compared, the effects of the anodizing and sealing process on the chemistry of the surface begin to emerge. As can be expected, the ESCA spectrum shows strong signal peaks for both aluminum and oxygen. These obviously result from the aluminum oxide that is formed during the anodizing process. Signal peaks are shown for chromium. These are much greater than expected if the source of the chromium was only from the material from which the specimen in the base was made. The chromium peaks obtained are probably due to the presence of chromium absorbed from the anodizing bath. The slight decrease in the chromium content of the sealed specimen (2 P₃ peak) suggests that the soaking in the hot sealing solution removed some of the

chromium from the surface. The weak peak shown for silicon (which is probably of a higher concentration than chromium in the bulk alloy and is essentially insoluble in the processing solutions) contributes to the proposition that much of the chromium detected was absorbed from the electrolyte during the anodizing process. Copper was not detected in the surface. This is surprising since a fairly high concentration (4 to 5%) of this material is present in the aluminum alloy. The failure to detect copper indicates that the copper is dissolved out of the surface during the cleaning and anodizing process. The same is true for magnesium. No trace of this material was detected even though it was present (1 to 2%) in the aluminum alloy. Only a very slight trace of manganese was detected in the sealed specimen; none in the unsealed specimen. This material was probably of a higher concentration than silicon in the alloy; thus, like copper and magnesium, it must have been selectively etched out of the surface during processing. The presence of iron and zinc was not detected.

Two elements (which were not present in the base alloy and not part of the final processing solutions) were strongly detected. The strongest, carbon, was present on the surface of both unsealed and sealed specimens. The structure of the peak strongly suggests that much of the carbon detected was in the form of carbonate, although hydrocarbon was also probably present. The source of the carbonate was probably carbon dioxide from the air. The second element found was nitrogen. The structure of the nitrogen peak did not rule out the presence of amine compound on the surface. The presence of an amine could also account for some hydrocarbon contamination. The source of the nitrogen was probably amine contamination of the deionized water which was obtained from a commercial resin bed deionizer, and used to rinse and seal the finished specimen. This supposition was supported by the great increase in the nitrogen signal obtained when the specimen was sealed by immersing it in a very dilute hot solution of chromic acid in deionized water.

When all the peak signal intensities for the sealed and unsealed specimens were compared, the intensities of the sealed specimens were always greater (except for chromium). The cause of this effect has not been determined although this effect is consistent enough to be significant.

Auger Electron Spectroscopy

Anodized specimens both sealed and unsealed were submitted to The Center for Surface and Coatings Research at Lehigh University for an auger electron spectroscopic analysis. After analysis it was reported that there was no major difference detected in the surface composition of the sealed and unsealed specimens. The surface layer (5 to 25 angstroms deep) consisted of aluminum, oxygen, chromium, and carbon. A copy of The Center's report is included as an appendix.

These results confirmed the presence of the above named elements, but did not detect the presence of nitrogen, silicon, and manganese which were detected as being present at lower concentrations by ESCA.

EXPERIMENTAL PROCEDURES

Materials

Aluminum

The specimens were cut from 1.7-mm-thick 2024-T3 aluminum alloy sheet into 25 by 100 mm strips. These were processed and used for the TEM and Auger electron spectroscopy. Since the ESCA instrument required a cylindrical specimen 11 mm in diameter and 19 mm long, these were machined from 13 mm cylindrical stock 2024-T4 alloy. The T3 temper material was not available in this size.

Chemicals

All chemicals used were of the chemically pure grade with the exception of the sodium dichromate and chromic acid, which were technical grade, and the alkaline cleaner, which was a proprietary product. The alkaline cleaning material was non-inhibited and etched the alloy during the cleaning cycle.

Surface Preparation of Specimens

Degreasing

The surfaces of the specimens were wiped with a clean acetone-saturated paper towel until they were free of all oil, grease, and marking ink.

Alkaline Cleaning

The degreased specimens were immersed in the alkaline cleaner at 11 grams per liter and 60°C for 5 minutes. The specimens were then rinsed with flowing tap water to remove all traces of cleaning solution. Specimens for TEM study were flushed with deionized water, then blown dry with a jet of dry filtered compressed air.

Deoxidizing

The alkaline-cleaned specimens were immersed in a solution (FPL) consisting of 33 1/3 grams of sodium dichromate ($\text{Na}_2 \text{Cr}_2 \text{O}_7 \cdot 5 \text{H}_2\text{O}$), 181 milligrams of concentrated sulfuric acid (Sg 1.84), and one liter of deionized water at 65°C for 9 to 11 minutes. The specimens were then flushed with flowing tap water to remove all traces of deoxidizer. Specimens for TEM study were flushed with deionized water, then blown dry with a jet of dry filtered compressed air.

Anodizing

The deoxidized specimens were made the anode in a 10% solution of chromic acid (Cr O_3) in deionized water at $35 \pm 1^\circ\text{C}$. The anodizing voltage sequence was (in order):

- 7½ volts for the first 2½ minutes
- 11½ volts for one minute
- 16½ volts for one minute
- 23 volts for one minute
- 30 volts for one minute
- 35 volts for one minute
- 40 volts for 30 minutes

When anodizing was terminated, the specimens were promptly removed from the anodizing solution and flushed with flowing tap water, then with deionized water. Specimens for TEM, ESCA, and Auger electron spectroscopic study were blown dry with a jet of dry filtered compressed air.

Sealing

The anodized specimens were immersed in a bath (100 ppm chromic acid in deionized water) at 82°C for 8 minutes. The specimens were flushed with deionized water to remove all traces of sealing solution and blown dry with a jet of filtered compressed air.

Transmission Electron Microscopy

Replication of Specimens

All surfaces were replicated within 24 hours after processing was completed. The specimens were stored in kraft paper envelopes until replicated. Unless stated otherwise, the specimen was placed in a vacuum evaporator and a 1/2-inch length of 8-mil platinum palladium wire was evaporated onto the surface from an approximate distance of 15 centimeters at an angle of about 30°. The specimen was then coated with carbon at an angle of 90° to the surface using a rotating stage. The surface of the coated specimen was scored in 2 x 2 mm squares and the replicas were freed from the surface by etching. A solution of one part by volume of Kellers Etch Conc., (Table 3) two parts by volume of concentrated nitric acid, and four parts deionized water was used to dissolve the metal underneath the evaporated platinum carbon replica. When the replicas floated free, they were rinsed and mounted on TEM grids. These were single-stage replicas.

Two-stage replicas were made as follows: An impression of the surface was obtained using polyvinyl acetate replicating tape softened with acetone. The softened tape was pressed against the surface and allowed to dry. It was then removed and placed in a vacuum evaporator where it was coated with platinum palladium and carbon, as described above. The coated plastic was cut into 2 x 2 mm squares and the plastic was removed by washing with acetone. The two-stage replicas were then mounted on TEM grids.

Specimens for ESCA and Auger

The specimens for spectroscopic analysis were machined to fit the instruments, then anodized and sealed as previously described.

CONCLUSIONS

1. The surface topography developed during each of the processing steps used to chromic-acid anodize and seal a surface is different when studied with the transmission electron microscope at 100,000 times magnification.
2. The topography of both degreased and alkaline-cleaned surfaces does not consist of a repetitive pattern of close packed depressions, but of a random distribution of hills, hollows, and crests. These surfaces are not used to form durable adhesive bonds.
3. The topography of (FPL) deoxidized, unsealed anodized and sealed anodized surfaces consists of a repeating pattern of close packed depressions. The depressions in the deoxidized surface are cup shaped with essentially perpendicular walls, 400 to 800 angstrom units in diameter. Those in the unsealed anodized surface are cone shaped, 200 to 400 angstrom units in diameter, and those in the sealed anodized surface are crevices 500 to 2000 angstrom units wide between mounds of material formed during sealing.
4. The topography of the unsealed chromic-acid anodized surface develops during the first 6 minutes of anodizing. No additional changes in surface structure were noted during the remainder of the anodizing cycle.
5. The topography of a sealed anodized surface forms during the latter half of the sealing cycle. No observable changes occurred until after the first half of the cycle.
6. The chemical composition of chromic-acid anodized sealed and unsealed surfaces consists of aluminum, oxygen, chromium, carbon, and nitrogen with traces of silicon and manganese. Copper and magnesium, two of the major alloying elements in the alloy used, were not detected.

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Table 1

Results of ESCA studies

Binding peak energy (EV)	Element	Intensity*	
		Unsealed specimen	Sealed specimen
645	Manganese 2P ₃	None detected	VVV weak
586	Chromium 2P ₁	Moderate	Moderate
577	Chromium 2P ₃	Weak	V weak
533	Oxygen 1S	VV strong	VVV strong
399	Nitrogen 1S	VV weak	Strong
285	Carbon 1S	Moderately strong	Strong
154	Silicon 2S	V weak	Weak
120	Aluminum 2S	Strong	V strong
80	Aluminum 2P	V strong	VV strong
28	Oxygen 2P	V strong	VV strong

*V = very

Table 2

Chemical composition of 2024 alloy

Element	%
Cu	3.8-4.9
Mg	1.2-1.8
Mn	0.3-0.9
Si	0.5 Max
Fe	0.1 Max
Cr	0.25 Max
Zn	0.05 Max
Other elements	0.15
Al	Remainder to make 100%

Table 3

Composition of Keller's etch concentrate

Amount	Component
10 ml	48% Hydrofluoric acid conc
15 ml	37% Hydrochloric acid conc
25 ml	70% Nitric acid conc
50 ml	De-ionized water



Fig 1 TEM of acetone-degreased surface
(6,750 x magnification)

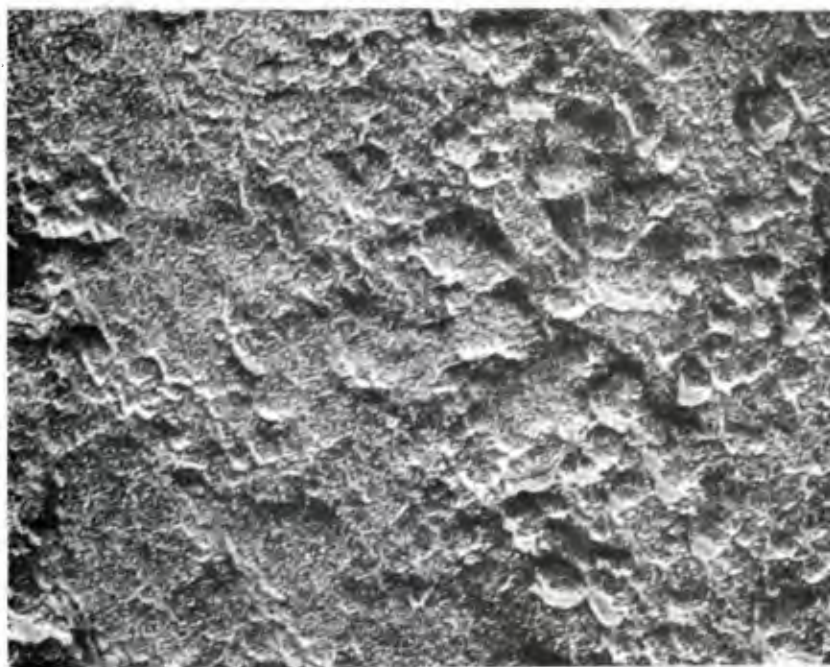


Fig 2 TEM of acetone-degreased surface
(100,000 x magnification)

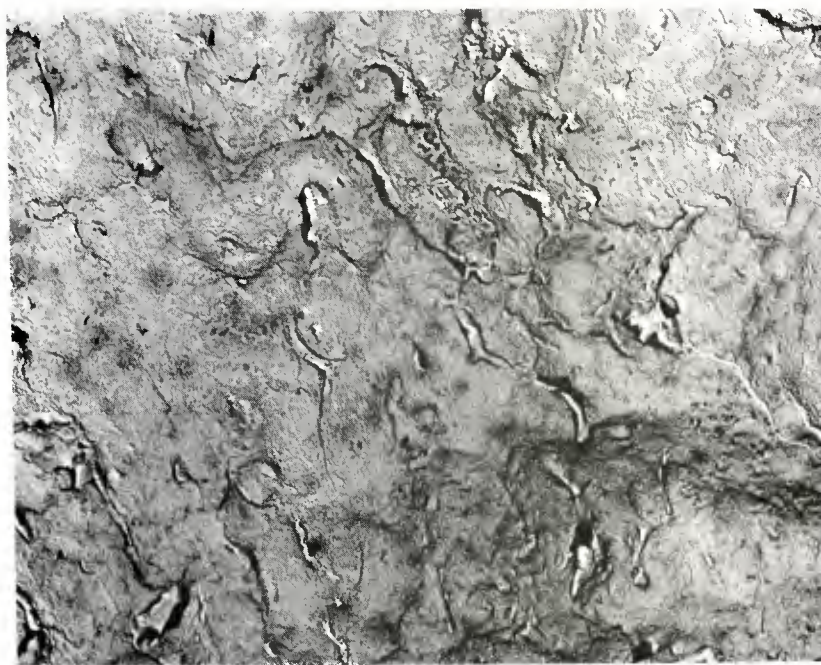


Fig 3 TEM of alkaline -cleaned surface
(6,750 x magnification)

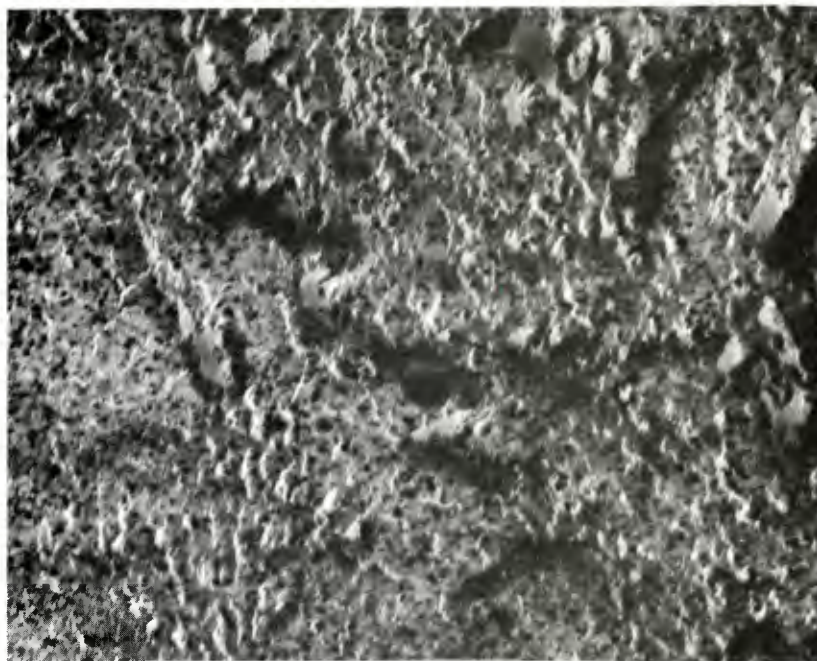


Fig 4 TEM of alkaline-cleaned surface
(100,000 x magnification)



Fig 5 TEM of (FPL) deoxidized surface
(6,750 x magnification)



Fig 6 TEM of (FPL) deoxidized surface
(100,000 x magnification)



Fig 7 TEM of surface chromic-acid anodized
for 2 minutes at $7\frac{1}{2}$ volts
(100, 000 x magnification)



Fig 8 Surface chromic-acid anodized
for $2\frac{1}{2}$ minutes at $7\frac{1}{2}$ volts
(100, 000 x magnification)



Fig 9 Surface chromic-acid anodized for
5½ minutes (100,000 x magnification)

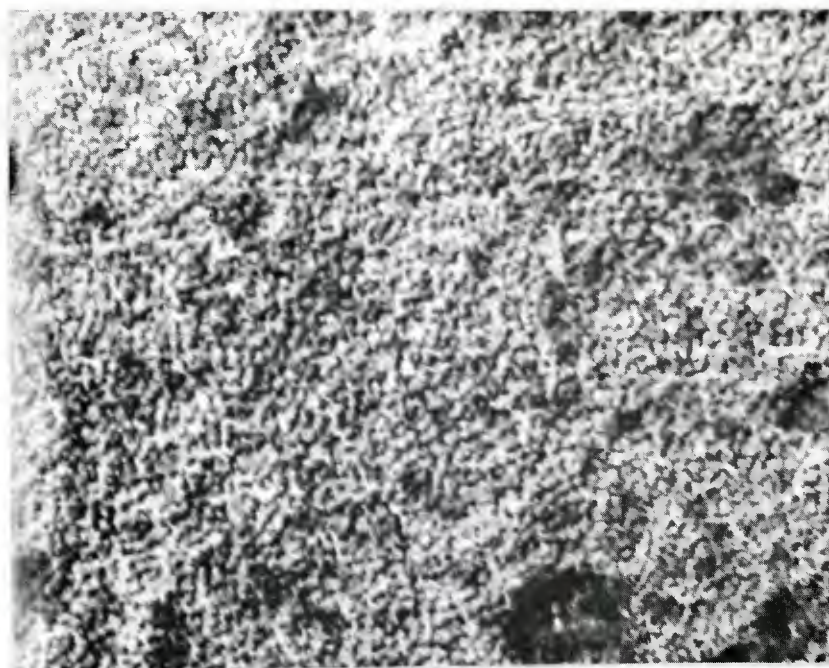


Fig 10 Surface chromic-acid anodized for
full cycle (100,000 x magnification)

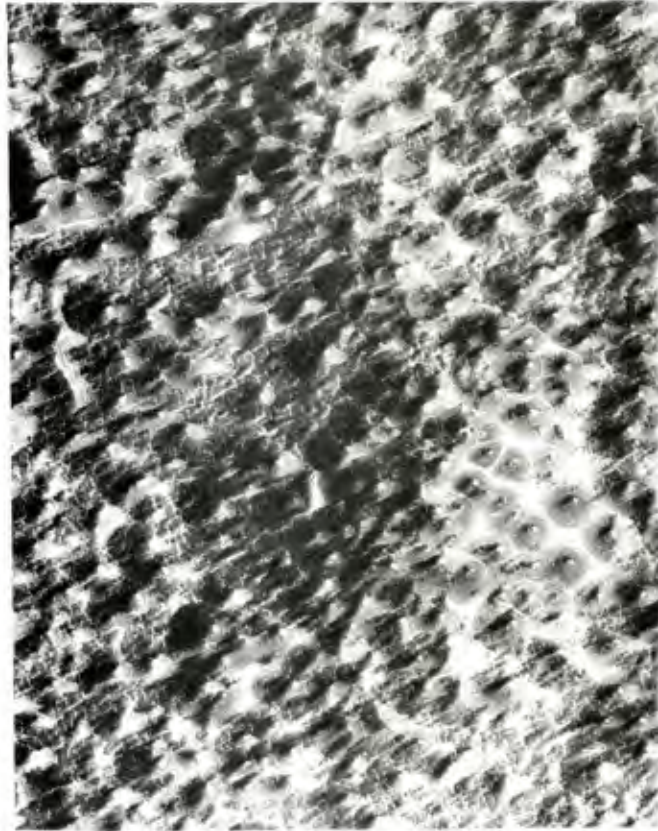


Fig 11 Two-stage replica of chromic-acid anodized surface showing internal structural pores (100,000 x magnification)

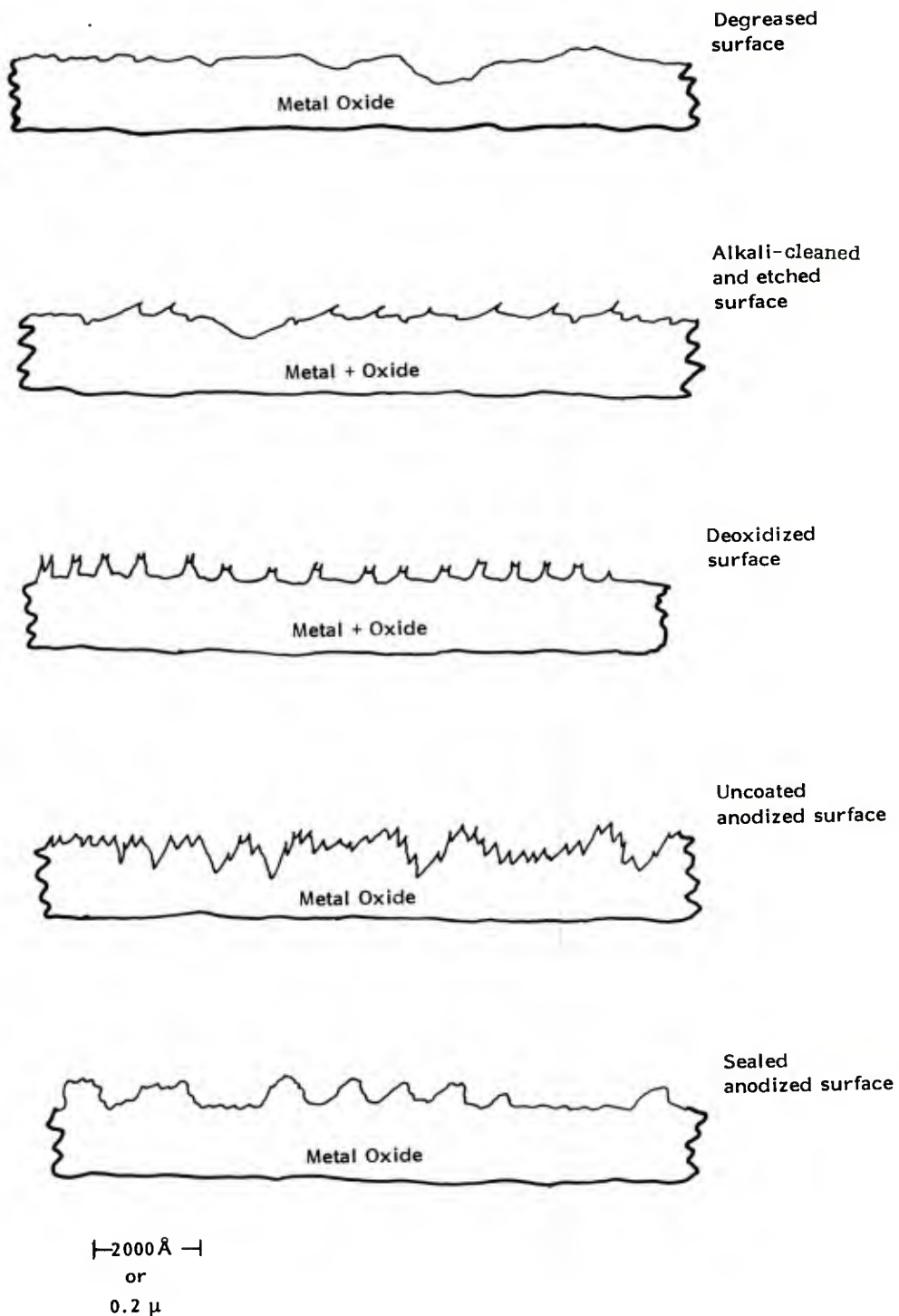


Fig 14 Sketched profiles of treated surfaces (to scale)



Fig 12 Sealed chromic-acid anodized surface (70,000 x magnification)

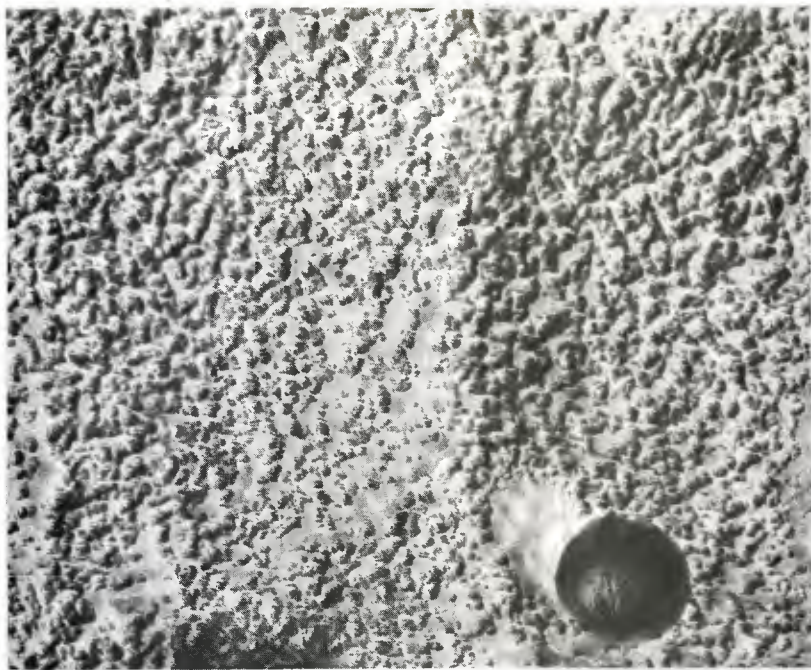


Fig 13 Sealed chromic-acid anodized surface (33,000 x magnification)

APPENDIX

**AUGER ELECTRON SPECTROSCOPIC ANALYSIS
OF ANODIZED ALUMINUM**

**Prepared
by
G. W. Simmons**

**Center for Surface and Coatings Research
Lehigh University, Bethlehem, Pennsylvania**

Objective of Analysis

The principal objective of the analysis was to compare the surface composition of two anodized aluminum specimens. One specimen was in the as anodized condition and the other was anodized and then sealed in a chromate bath.

Experimental Procedure

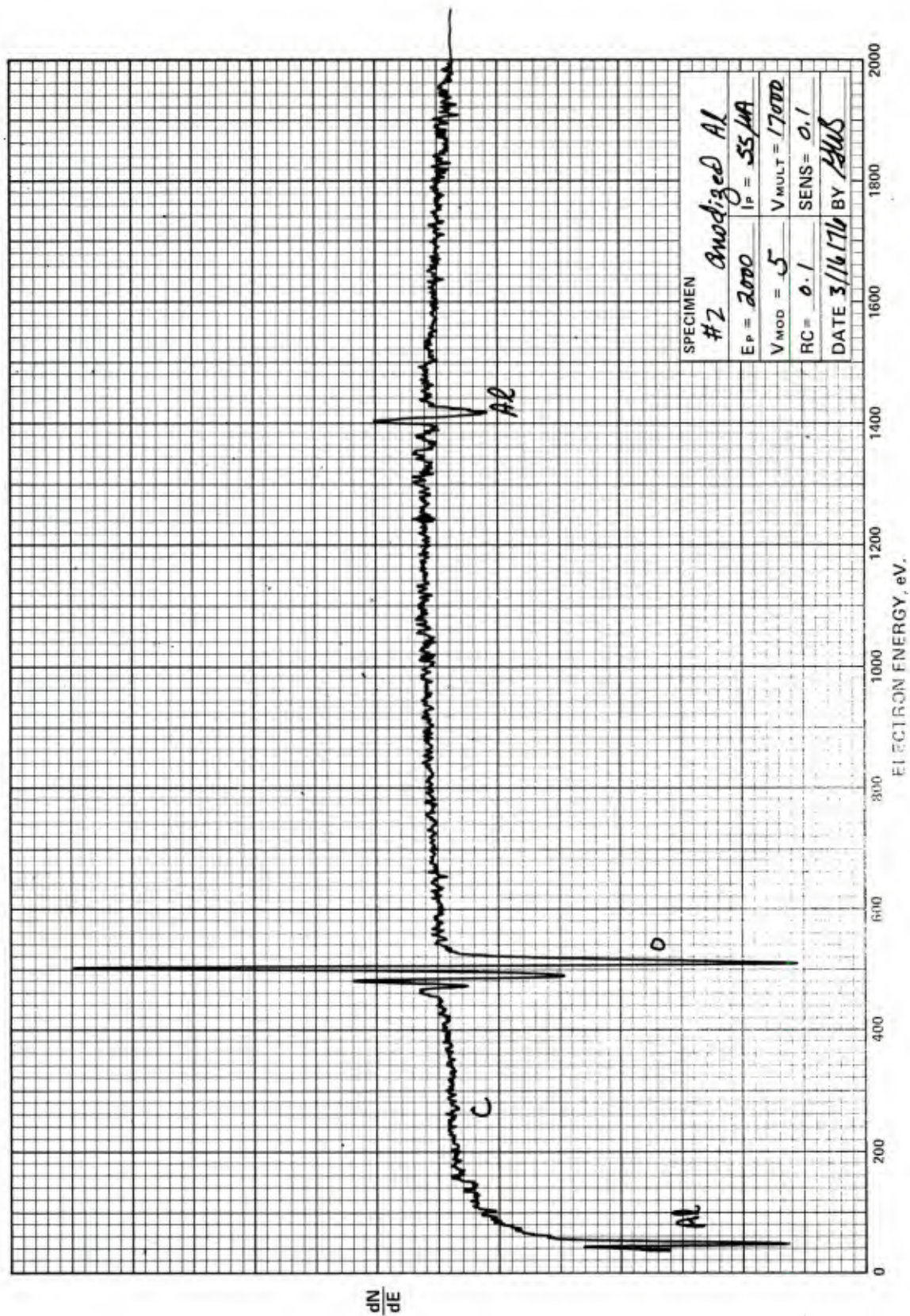
The specimens were mounted in the spectrometer directly as received from Mr. Russell of Picatinny Arsenal. Although the aluminum oxide surface is dielectric, no interference due to surface charging was encountered. The area of the specimen surface represented by the spectra is determined by the 0.5 mm diameter of the incident electron beam. The sensitivity of the Auger electron spectroscopy technique is on the order of one atomic percent, and the escape depth of Auger electrons varies from 5 to 25 Angstroms over the energy range of 0-2000 eV.

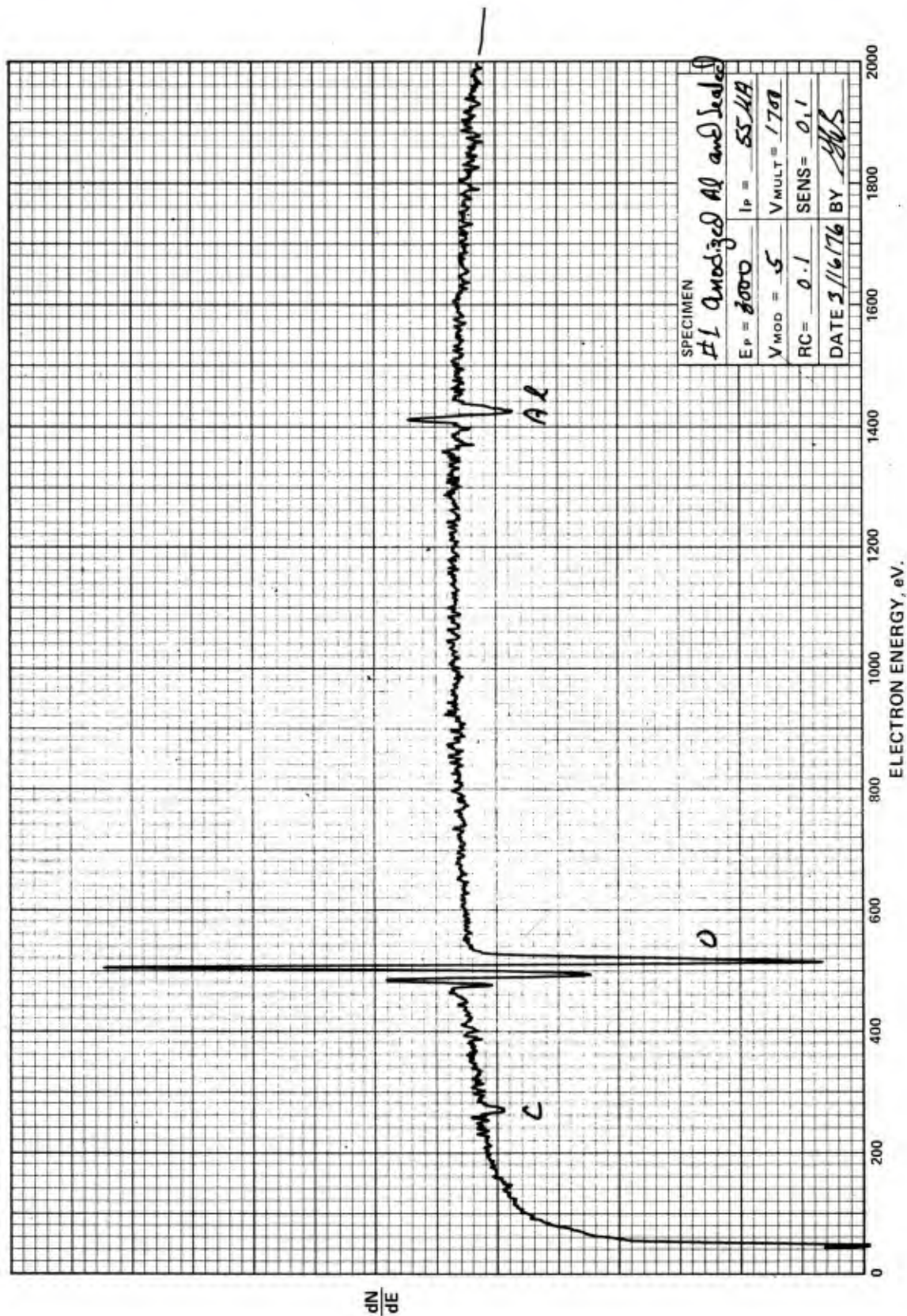
Results of Analysis

Spectra taken of the two specimens have been included in the report for reference. No major differences were observed for the surface composition of the anodized and anodized-sealed specimens. Carbon was the only element found in addition to oxygen and aluminum expected for the oxide. The amount of carbon was approximately the same for both specimens.

It is interesting to note that if chromium is present on the surface of the sealed specimen, the concentration is too low to be resolved in the spectrum. Unfortunately, the sensitivity for chromium in the presence of oxygen is reduced owing to the overlap in energy of the chromium and oxygen Auger electron transitions.

The specimens may be different in their degree of hydration, but it is not possible to make conclusions of this fact from these Auger electron spectra.





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